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(54) CYCLOALKANE DERIVATIVE, CARBOXYLIC ACID DERIVATIVE AND CUT-FLOWER FRESHNESS-PRESERVING AGENT USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a novel compound which is useful as a cut-flower freshness-preserving agent.

SOLUTION: This novel compound is represented by formula I (R1 is a 1-8C alkyl, phenyl, phenethyl, styryl), typically 1-benzoylaminomethyl- cyclopropanecarboxylic acid. The compound of formula I can be produced through a variety of routes, but usual amidation reaction can be applicable in the case that 1-aminomethylcyclopropanecarboxylic acid is used as a starting substance. For example, 1-aminomethylcyclopropanecarboxylic acid is allowed to react with an acid halide of the formula: R1COX (X is a halogen), preferably in the presence of a base (for



I



II

example, NaOH) in a solvent (for example, toluene) at -20-100°C for 0.1-24 hours. The compound of the formula is inexpensive, has high retention effect of flower freshness, reduces the load to environments with low occurrence of phytotoxicity. In addition to the compound of formula I, 1-cyano-cyclopropanecarboxylic acid, compounds of formula II (R2 is H, a 1-11C alkylcarbonyl or the like) may be preferably used.

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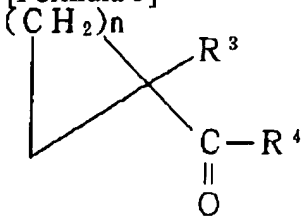
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DETAILED DESCRIPTION

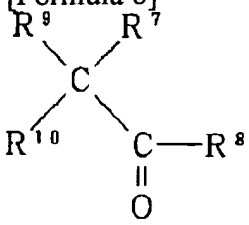
[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the new compound of the freshner for cut flowers which used the cycloalkane derivative, the carboxylic-acid derivative, this derivative, etc., and these freshners, or its salt.
[0002]
[Description of the Prior Art] A petal and a leaf will wither, ****** will advance as a freshness fall begins from immediately after flower-gathering and cut flowers follow a day, and appreciation worth of **** will be lost soon. For example, if 10 day will pass from one week after harvest in the carnation currently consumed 700 million per year also in cut flowers, a petal will age rapidly with the rapid increment in endoecism ethylene (withering). In the flowering plant industry, prevention of freshness degradation of the cut flowers to which need will be expanded increasingly from now on is a very important technical problem, and in order to solve this technical problem, various freshners are used. For example, the carnation which has appeared on the market in the commercial scene in recent years is processed for the purpose of freshness maintenance with the thiosulfuric-acid silver which is an ethylene operation inhibitor. Thiosulfuric-acid silver is used to many ethylene susceptibility cut flowers besides the carnation, and it can be said that it is an indispensable freshner in current flowering plant industry
[0003]
[Problem(s) to be Solved by the Invention] However, thiosulfuric-acid silver contains the complex ion which is a heavy metal ion, and, also internationally, development of the alternative freshner by which the environmental load was reduced due to concern of the environmental pollution by complex ion is called for in recent years. Development of various freshners is made in order to replace the basis of this background, and thiosulfuric-acid silver, and the alpha-aminoisobutyric acid, an AROKORONAMIN acid, or cis-propenyl phosphonic acid is proposed as a freshner for cut flowers until now. However, the alpha-aminoisobutyric acid is very expensive and lacking in practicality, and since an AROKORONAMIN acid is difficult to compound, it is difficult to industrialize. Moreover, cis-propenyl phosphonic acid is not put in practical use from there being phytotoxicity of a leaf etiolating. That is, the present condition is that what an environmental load is reduced compared with thiosulfuric-acid silver, and generating of phytotoxicity can moreover still satisfy enough industrially few as a freshner which can be manufactured is not obtained. The technical problem of this invention has the high freshness maintenance effectiveness of cut flowers, and the load to an environment is mitigated, and it is cheap and is in moreover offering the new compound of the freshner for cut flowers with little generating of phytotoxicity, and these freshners, or its salt.
[0004]
[Means for Solving the Problem] This invention relates to the new compound of the freshner for cut flowers characterized by the thing which is chosen as the carboxylic-acid derivative list expressed with the cycloalkane derivative and general formula (4) which are expressed with a general formula (3) from these salts, and which contain a kind as an active principle at least, and these freshners, or its salt

[0005]
[Formula 5]



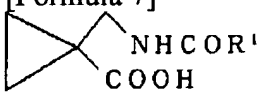
(3)

(n shows 1 or 2 among a formula, and R3 show a hydrogen atom, the amino group, a cyano group, -C (O) R5, or CH2-NHR6.) R4 shows a hydroxyl group, C1 - 4 alkoxy groups, the amino group, or an ANIRINO radical. R5 shows a hydroxyl group, C1 - 4 alkoxy groups, or the amino group. R6 shows a hydrogen atom, C1 - 11 alkyl carbonyl group, phenethyl carbonyl, styryl carbonyl, or benzoyl. However, R4 is not a hydroxyl group, when n is 1 and R3 are an amino group.
[0006]
[Formula 6]



(4)

(R7 shows a cyano group, the amino group, or C1 - 4 alkoxy carbonyl group among a formula.) R8 shows a hydroxyl group, or C1 - 4 alkoxy groups. R9 and R10 are the same -- or it differs and a hydrogen atom, or C1 - 4 alkyl groups is shown.
[0007]
[Embodiment of the Invention] Said general formula (1) In the compound of - (4), the example of each radical shown by R1-R10 is as follows. As C1 - 4 alkyl groups, methyl, ethyl, propyl, isopropyl, cyclo propyl, butyl, isobutyl, sec-butyl, tert-butyl, cyclo butyl, etc. are mentioned. In addition to said C1 - 4 alkyl groups, as C1 - 8 alkyl groups, pentyl, hexyl, cyclohexyl, heptyl, an octyl radical, etc. are mentioned. In addition to said C1 - 4 alkyl groups, and said C1 - 8 alkyl groups, nonyl, DESHIRU, an undecyl radical, etc. are mentioned as C1 - 11 alkyl groups. As C1 - 4 alkoxy groups, methoxy and ethoxy ** propoxy, isopropoxy, and a butoxy radical are mentioned. As C1 - a 4 alkoxy carbonyl group, methoxycarbonyl, ethoxycarbonyl, propoxy carbonyl, isopropoxycarbonyl, a butoxycarbonyl radical, a tert-butoxycarbonyl radical, etc. are mentioned. As a salt, sodium salt, potassium salt, ammonium salt, a hydrochloride, a sulfate, etc. can be illustrated. Although some of said compounds were known compounds, they were not known about all having the freshness maintenance effectiveness to cut flowers. Moreover, it is as follows reference a non-indicated compound among said compounds. The compound expressed with a general formula (1), and its salt (compound of claim 1).
[0008]
[Formula 7]



(1)

(R1 shows C1 - 8 alkyl groups, a phenyl group, a phenethyl radical, or a styryl radical among a formula.)
[0009] The compound of a general formula (1) is compounded by the amidation reaction usually performed, when it can manufacture by various approaches and 1-aminomethyl cyclopropane carboxylic acid is used as starting material. For example, it is acid halide to 1-aminomethyl cyclopropane carboxylic acid. R1COX (inside of a formula [R1 is the same as the above.]) X shows a halogen atom

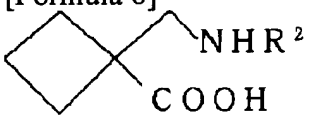
The approach of making it react is mentioned. Usually, about 0.5-5 mols of latters are used to one mol of former. In this reaction, it is desirable to make a base live together in order to remove the halide acid to generate. As a base to be used, a well-known thing can be used widely conventionally, for example. organic metal bases, such as inorganic bases, such as organic bases, such as triethylamine, pyridine, 4-N, and N-dimethylamino pyridine and N.N-dimethylaniline, a sodium hydroxide, and potassium carbonate. butyl lithium, and a lithium diisopropyl amide, sodium acetate, etc. can be illustrated. Moreover, although it changes also with classes of base used as a solvent Generally an inert solvent is desirable For example, aromatic hydrocarbon, such as benzene, toluene, and a xylene Pyridines, such as a pyridine and picoline, dichloromethane, chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane, tetrachloroethylene, Halogenated hydrocarbon, such as a trichloroethylene, chlorobenzene, and o-dichlorobenzene Ether, such as aprotic polar solvents, such as aliphatic hydrocarbon, such as n-hexane N.N-dimethylformamide, and dimethyl sulfoxide, diethylether, a tetrahydrofuran, and dioxane, water, or these mixed solvents are mentioned. -20-100 degrees C, preferably, this reaction is a temperature requirement 0 degree C - near a room temperature, and is usually ended in about 0.1 - 24 hours.

[0010] 1-cyano cyclopropane phenyl amide (compound of claim 2).

This compound is manufactured by the amidation reaction usually performed, when it can manufacture by various approaches and 1-cyano cyclopropane carboxylic acid is used as starting material. For example, the approach to which the acid halide which inorganic halogenides, such as a phosphoryl chloride, a thionyl chloride, a phosphorus pentachloride, and a phosphorus trichloride, are made to act. and is obtained in 1-cyano cyclopropane carboxylic acid, and an aniline are made to react is mentioned. The base and solvent which are used for a reaction, the amount of the reaction agent used, reaction temperature, and reaction time are the same as that of the above-mentioned amidation reaction. At the reaction of acid halide and an aniline, by using an aniline more than the amount of 2 double, even if it does not use a base in addition to this, it can manufacture. The compound expressed with a general formula (2), and its salt (compound of claim 3).

[0011]

[Formula 8]



(2)

(A hydrogen atom, C1 - 11 alkyl carbonyl group, a styryl carbonyl group, or benzoyl is shown by the inside R2 of a formula.)

[0012] R2 among the compounds of a general formula (2) The compound (1-aminomethyl cyclobutanecarboxylic acid) which is a hydrogen atom is compounded by the reduction reaction of nitril usually performed, when it can manufacture by various approaches and 1-cyano cyclobutanecarboxylic acid is used as starting material. For example, it is manufactured by using metallic hydrogen complex compounds, such as a lithium aluminum hydride, for 1-cyano cyclobutanecarboxylic acid, or carrying out contact hydrogenation using the catalyst of a Raney nickel catalyst, Raney cobalt, diacid-ized platinum, etc. In the reduction reaction using a metallic hydrogen complex compound, ether, such as diethylether and a tetrahydrofuran, is usually used for a solvent, and a desiccation solvent is desirable. In the contact hydrogenation reaction using a catalyst etc., alcohol, ammonia saturated alcohol, an acetic acid, etc. are usually used for a solvent. R2 R2X among the compounds of a general formula (2) C 1-11 The compound which is an alkyl carbonyl group, a styryl carbonyl group, or benzoyl is acid halide to 1-aminomethyl cyclobutanecarboxylic acid. (inside of a formula [R2 is the same as the above.]) X A halogen atom is shown. It can manufacture by making it react. The solvent to be used, a base, reaction temperature, reaction time, etc. are the same as that of the time of manufacture of the compound shown by the above-mentioned general formula (1).

[0013] Among the compounds used as an active principle of the freshner of this invention, the thing except said and its salt are known compounds, are commercially available or can be easily obtained to J.Chem.Soc., 75,921-927 (1899), etc. by the approach of a publication etc. The freshner of this invention

is manufactured by dissolving the above-mentioned active principle in a suitable solvent with a suitable surfactant and other suitable components if needed. Although the freshner of this invention can be used with the gestalt of a water solution, organic solvents, such as ethanol, may be used for it and it may usually use these together. Moreover, medicine is manufactured by the shape of powder, granularity, and a tablet, and at the time of use, it may be made to dissolve in water and you may use. Although the concentration of an active principle is suitably defined according to conditions, such as a class of object flowering plant, an art, and the processing time, it is usually 0.1-100mM, and in the case of after treatment, it is desirable to make it into 1 - 100mM extent in 0.1 - 50mM and pretreatment.

[0014] As a surface active agent which can be used for the freshner of this invention, alkylbenzene sulfonates, fatty alcohol sulfate, alkyl trimethylammonium chloride, a betaine mold compound, sodium lauryl sulfate, a naphthalene formaldehyde condensate, polyoxyethylene sorbitan monooleate, polyoxyethylene SUCHIRIRUE-Tell, polyoxyethylene RAURIRUE-Tell, polyoxyethylene nonyl phenyl ether, a polyoxyethylene polyoxypropylene blockpolymer, sucrose fatty acid ester, etc. are mentioned, for example. As concentration of a surfactant, although suitably set by the class, the object flowering plant, the art, and the processing time of a surfactant, generally in the case of after treatment, in about 3-1000 ppm and pretreatment, it is about about 3-300 ppm. Moreover, the freshner of this invention can be made to contain the component of sedimentation agents, such as pH regulators, such as plant growth regulators, such as parts for micronutrient, such as nutrients, such as nitrogen, Lynn, a potassium, and cane sugar, iron, zinc, manganese, copper, and boron, B-nine (DAMINOJIDO), and a benzyladenine, and a sodium hydrogencarbonate, and an aluminum sulfate, other freshners, a color coupler, a germicide, antiseptics, and others.

[0015] On the occasion of use of the freshness processing agent of this invention, that what is necessary is just to immerse the cut end of cut flowers in the freshner of this invention, since special processing is not needed, anyone can carry out in various scenes easily. The method of keeping [immerse / in this invention freshner / the cut end of cut flowers] made or the approach in which only fixed time amount is made immersed is more specifically mentioned. The former is an approach called the so-called after treatment adopted when arranging cut flowers in the vase at the case where cut flowers are very sold to containers, such as a bucket, at a store etc., the home, the exhibition, etc., and the latter is an approach by which a flowering plant production contractor is called after [harvest] fixed time amount, for example, the so-called pretreatment as which it is adopted when performing drugs processing for about 4 to 24 hours and shipping after that. In addition, the freshner of this invention can be used by the leaf. spray processing to a petal, etc.

[0016] Although there is especially no limit as object flowering plants of the freshner of this invention and it is effective in various kinds of flowering plants For example, a carnation, SUITOPI -, SUKASHIYURI, a European monkshood, A butterfly weed, HANATORANOO, Delphinium, HANAAOI, contribution NYURA, A bleeding heart, a veronica, you FORU beer full GENSU, astro-MERIA, A freesia, a mustached pink, snapdragon, a gypsy rose, a stock, When it uses for Gypsophila elegans, a bougainvillea, a geranium, KARUSE ora rear ** ******, ****-****, BUBARUDIA, grotesque RIOSA, cosmos, RISHIANSASU, a dahlia, a fuchsia, SANTAKA, etc., remarkable effectiveness is especially done so.

[0017]

[Example] The example of reference, the example of manufacture, and the example of a trial are given to below, and this invention is explained to it still more concretely.

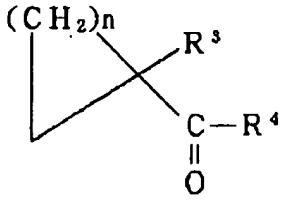
Example 1 of reference Contact hydrogenation of the 1-cyano cyclopropane carboxylic-acid (2)1g (9 millimol) was carried out in ordinary temperature and ordinary pressure under diacid-ized platinum existence for 30 hours among the synthetic acetic-acid solvent of 1-aminomethyl cyclopropane carboxylic acid (10). Cerite filtration of the reaction mixture is carried out, vacuum concentration of the toluene is added and carried out to filtrate, and it is a yellow rough crystal. 1.4g was obtained. This thing was ******ed from the methanol and the 538mg colorless crystal was obtained. (52% of yield) The melting point [a reference value and 238 degrees C (decomposition)] of 235 degrees C (decomposition) IR(KBr) numax(cm-1):3250-2250 (NH3+), 1620 (deltaasNH3+), 1570 (nuasCOO-), 1520

(deltaasNH3+), 1400 (nusCOO-), 1250 and 1110, 8601 H-NMR(CD3OD):delta0.69-0.72 (2H, m), and 1.16- 1.19 (2H, m) and 3.30 (2H, s, CH3)
[0018] Example 1 of manufacture Synthetic 1-cyano cyclopropane carboxylic-acid (2)1.67g and the thionyl chloride of 1-cyano cyclopropane phenyl amide (5) 15ml was mixed and the heating ring current was performed for 4 hours. To this solution, it is anhydrous toluene. Aniline dissolved in 30ml 4.0g (43 millimol) was added and heating churning was carried out for 1 hour. Then, water was cooled and poured and the organic layer was washed in order of a hydrochloric acid, 10% sodium hydroxide, and water 5%. It dried, vacuum concentration of the organic layer was carried out, and the brown rough crystal was obtained. It recrystallized [toluene] and the 0.30g colorless crystal was obtained. (11% of yield)
Melting point 90 degree-CIR(KBr) numax(cm-1):3250(NH), 3050 and 2240 (CN), 1670 (C=O, amide), 1600, 1540, 1490, 1450, 1330, 1250, 1180 and 1080, 9701 H-NMR(CD3OD):delta1.60-1.72 (4H, m), 7.13-7.54 (5H, m, Ph)
[0019] Example 2 of manufacture Acetic acid which added and distilled the acetic anhydride of 0.5% w/w of composition of 1-acetamido methyl cyclopropane carboxylic acid (11) It is diacid-ized platinum to 15ml. 20mg and 1-cyano cyclopropane carboxylic acid 1g (9 millimol) was added and contact hydrogenation was carried out over 30 hours in room temperature 1atm. A product is filtered, filtrate is condensed and it is a yellow rough crystal. 1.2g was obtained. This thing was ******ed from chloroform and the 353mg colorless crystal was obtained. (25% of yield)
Melting point 164 degree-CIR(KBr) numax(cm-1):3600-2300 (COOH), 1710 (C=O, carboxyl), 1680 (C=O, amide), 1540, 1400, 1260 (C-N), 1130 (C-O)
1 H-NMR(CD3OD): 1.95 (3H, s, CH3) delta0.9-0.95 (2H, m), 1.18-1.22 (2H, m), 3.31 (2H, s, CH2)
[0020] Example 3 of manufacture The tetrahydrofuran was added and agitated to synthetic 1-aminomethyl cyclopropane carboxylic acid (10) of 1-benzoyl aminomethyl cyclopropane carboxylic acid (21). It is water to this. Sodium hydroxide dissolved in 3.41ml 1.37g is added, and it continues and is a benzoyl chloride. 2.11ml was added. After agitating for 30 minutes at a room temperature, concentrated hydrochloric acid was added at 0 degree C, it was made acidity, and ethyl acetate extracted after irrigation. The organic layer was doubled, saturation brine washed and it was made to dry with sulfuric anhydride magnesium. Vacuum concentration is carried out and it is a light yellow rough crystal. 2.88g was obtained. This was ******ed from the hexane-ether and the 1.31g crystal was obtained.
Melting point 190-190.5 degree-CIR(KBr) numax(cm-1):3370(NH), 3200- 2500 (COOH) and 1690 (C=O, carboxyl) -- 1610 (C=O, amide), 1540, 1420, 1240 (C-N), 1170 (C-O), 1030 (C-N), 9001 H-NMR(CD3OD):delta1.02 (2H, q, CH2), 1.23 (2H, q, CH2), 3.61 (2H, s, CH2), 7.40-7.53 (5H, m, C6H5)

[0021] It replaces with example of manufacture 4 benzoyl chloride. A chlorination propionyl, the chlorination n-butyryl, Chlorination isobutyryl, chlorination pivaloyl, chlorination 2-ethyl hexa noil, The phenylacrylyl chloride was used and also it is made to be the same as that of the example 1 of manufacture. 1-propionyl aminomethyl cyclopropane carboxylic acid (12), 1-butyryl aminomethyl cyclopropane carboxylic-acid (13) 1-isobutyryl aminomethyl cyclopropane carboxylic-acid (14), 1-pivaloyl aminomethyl cyclopropane carboxylic-acid (16) 1-ECHIRUHEKISANOIRU aminomethyl cyclopropane carboxylic-acid (18) and 1-cinnamoyl aminomethyl cyclopropane carboxylic acid (20) were manufactured.
[0022] 1-propionyl aminomethyl cyclopropane carboxylic acid (12)
Colorless crystal IR(KBr) numax(cm-1):3350(NH), 3050- 2850 (COOH) and 1690 (C=O, carboxyl) -- 1620 (C=O, amide), 1540, 1460, 1420, 1310, 1240 (C-N), 1180 (C-O), 1100, 1030, 960, 9201 H-NMR (CD3OD):delta1.07 (2H, m), 1.16 (3H, t, CH2), 1.32 (2H, m), 2.23 (2H, q, CH2), 3.42 (2H, d, CH2)
[0023] 1-butyryl aminomethyl cyclopropane carboxylic acid (13)
Colorless crystal IR(KBr) numax(cm-1):3300(NH), 3100 (COOH), 2950, 1620 (C=O, carboxyl), 1560 (C=O, amide), 1420, 1270, 1220 (C-N), 2.32 (2H, t, CH2) 1110, 1060, 1020, 905, 800, 770, 6101 H-NMR(CDCl3):delta0.96 (3H, t, CH3), 1.04-1.33 (4H, m), 3.41 (2H, d, CH2)

[0024] 1-isobutyryl aminomethyl cyclopropane carboxylic acid (14)
Colorless crystal IR(KBr) numax(cm-1):3340(NH), 2960-2870, and 2580- 2540 and 1680 (COOH) -- 1620 (C=O, amide), 1560, 1470, 1420, 1310, 1230, 1190, 1100 (C-N), 1040, 960, 900, 865, 750, 680. 5801 H-NMR(CDCl3):delta1.08 (2H, m), 1.16 (6H, d, 2CH3), 1.33 (2H, m), 2.36 (1H, m, CH), 3.42 (2H, d, CH2)
[0025] 1-pivaloyl aminomethyl cyclopropane carboxylic acid (16)
Colorless crystal IR(KBr) numax(cm-1):3350(NH), 2950, 2600, 1690 (C=O, carboxyl), 1640 (C=O, amide), 1530, 1450, 1420, 1360, 1340, 1290, 1260, 1200, 1080 (C-N), 1030, 950, 910, 850, 640, 5301 H-NMR(CDCl3):delta1.07 (2H, m), 1.20 (9H, s), 1.32 (2H, m), 3.42 (2H, d, CH2)
[0026] 1-ECHIRUHEKISANOIRU aminomethyl cyclopropane carboxylic acid (18)
colorless liquefied object IR(film) numax(cm-1): -- 3340 (NH), 3250-2700 (COOH), and 2250, 1700 (C=O, carboxyl), 1620 (C=O, amide), 1540, 1460, 1420, 1370 and 1180 (C-O)
1 H-NMR(CD3OD): 3.44 (2H, d, CH2) delta1.09 (2H, m, CH2), 7.28 (1H, br, OH)
[0027] 1-cinnamoyl aminomethyl cyclopropane carboxylic acid (20)
White crystalline melting point 245-255.5 degree-CIR(Kbr) numax(cm-1):3370(NH), 3250-2300 (COOH), 1680 (C=O, carboxyl), 1590 (C=O, amide), 1490, 1420, 1220 (C-N), 1170 (C-O)
1 H-NMR(CD3OD): delta0.99 (2H, q, CH2), 1.23 (2H, q, CH2), 3.52 (2H, q, CH2), 6.65 (H, s, CH), 6.72 (H, s, CH), 7.30-7.60 (5H, m, C6H5)
[0028] Example 5 of manufacture Contact hydrogenation of the 1-cinnamoyl aminomethyl cyclopropane carboxylic-acid (20) 0.5g (2 millimol) was carried out in a room temperature and 1atm under existence of the synthetic diacid-ized platinum catalyst of 1-phenyl propionylamino MECHIRUSHIKUROPUROPAN carboxylic acid (19), and in 7ml of acetic acids. 20 hours after, after filtering reaction mixture, vacuum concentration was carried out and the 247mg yellow crystal was obtained.
Melting point 41 degree-CIR(KBr) numax(cm-1):3370(NH), 3300-2300 (COOH), 1690 (C=O, carboxyl), 1620 (C=O, amide), 1540, 1420, 1240 (C-N), 1190 (C-O)
1 H-NMR(CD3OD): delta2.85 (2H, t, CH2), 2.95 (2H, t, CH2), 3.10 (2H, s, CH2), 7.10-7.30 (5H, m, C6H5)
[0029] Example 6 of manufacture Sequential addition of the synthetic diacid-ized platinum catalyst of 1-aminomethyl cyclobutanecarboxylic acid (24), 7ml (what was distilled simply) of acetic acids, and the 1-cyano cyclobutanecarboxylic acid (23) 1.0g (8 millimol) was carried out, and contact hydrogenation was carried out in a room temperature and 1atm. 25 hours after, after filtering reaction mixture, vacuum concentration was carried out and the 0.72g white crystal was obtained. (70% of yield)
Melting point 195-197 degreeCIR(KBr) numax(cm-1):3400-2280 (NH3+), 2180, 1620 (deltaasNH3+), 1560 (nuasCOO-), 1510 (deltasNH3+), 1390 (nusCOO-), 1250, 1180, 11301 H-NMR(D2O):delta1.88-2.05 (4H, m), and 2.32- 2.44 (2H, m) and 3.28 (2H, s, CH2)
[0030] Example 7 of manufacture Synthetic 1-aminomethyl cyclobutanecarboxylic acid (24) 0.5g (4 millimol) of 1-acetamide methyl cyclobutanecarboxylic acid (25), 0.61g (8 millimol) of acetyl chlorides, DMF10ml, and pyridine 10ml were added, and it agitated at the room temperature for 1 hour. Then, 3.5ml of concentrated hydrochloric acid was added by 0-degreeC, it was made acidity, 20ml of water was put in, and ethyl acetate extracted. The organic layer was doubled, it washed and dried, and vacuum concentration was carried out and the 0.35g yellow liquid was obtained. The column chromatography (10:1 - ethyl acetate: hexane: ethyl-acetate = methanol = 10:1) refined this thing, and the 0.19g colorless liquid (25) was obtained. (28% of yield)
Melting point 140-141 degree-CIR(Kbr) numax(cm-1):3360(NH), 3300-2400 (COOH), 1690 (C=O, carboxyl), 1630 (C=O, amide), 1555, 1420, 1205 (C-O), 710 (C-N)
1H-NMR(D2O):delta1.88- 2.02 (4H, m), 1.96 (3H, s, CH3), and 2.30- 2.43 (2H, m) and 3.57 (2H, s, CH2)
[0031] Replaced with the example of manufacture 8 acetyl chloride, and chlorination lauroyl, the phenylacrylyl chloride, and the benzoyl chloride were used, respectively, and also 1-lauroyl aminomethyl cyclobutanecarboxylic acid (26) 1-cinnamoyl aminomethyl cyclobutanecarboxylic acid

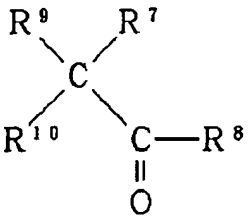
(27) and 1-benzoyl aminomethyl cyclobutanecarboxylic acid (28) were compounded like the example 7 of manufacture.
[0032] 1-lauroyl aminomethyl cyclobutanecarboxylic acid (26)
light yellow crystalline melting point 45degree-CIR(KBr) numax(cm-1): -- 3310 (NH), 3200-2700 (COOH), and 1700 (C=O, carboxyl), 1640 (C=O, amide), 1540, 1460, 1430, 1380, 1240 (C-N) and 1210 (C-O)
1 H-NMR(CD3OD):delta1.90-2.03 (4H, m) and 2.33- 2.42 (2H, m) and 3.32 (2H, m, CH2)
[0033] 1-cinnamoyl aminomethyl cyclobutanecarboxylic acid (27)
Melting point 125-126 degree-CIR(KBr) numax(cm-1):3340(NH), 3220-2720 (COOH), 1690 (C=O, carboxyl), 1610 (C=O, amide), 1550, 1420, 1390, 1210 (C-O), 670 (C-O)
1 H-NMR(CDCl3): delta1.91-2.09 (4H, m), 2.39-2.46 (2H, m), 3.32 (2H, s, CH2), 7.34-7.41 (5H, m, C6H5)
[0034] 1-benzoyl aminomethyl cyclobutanecarboxylic acid (28)
light yellow crystalline melting point 116-116.5degree-CIR(KBr) numax(cm-1): -- 3430 (NH) -- 1900 333-2720 (COOH), 1700 (C=O, carboxyl), 1630 (C=O, amide), 1530, 1400, 1240 (C-N), 1160 (C-O), 8901 H-NMR(CDCl3):delta1.89-2.14 (4H, m), 2.39-2.47 (2H, m), 3.32 (2H, s, CH2), 7.40-7.52 (5H, m, C6H5)
The typical compound which can be used as an active principle of the freshner for cut flowers of this invention is shown in Table 1 and 2. in addition, a table -- setting -- Me -- methyl and Et -- in ethyl and Pr, heptyl and cycl-Pr show cyclo propyl and, as for propyl and Bu, Ph shows phenyl, as for butyl and Hep.
[0035]
[Table 1]



(3)

化合物番号	n	R^3	R^4
1	1	H	OH
2	1	CN	OH
3	1	CN	OEt
4	1	CN	NH_2
5	1	CN	NHPh
6	1	COOH	OH
7	1	COOH	OEt
8	1	COOH	NH_2
9	1	COOEt	OEt
10	1	CH_2NH_2	OH
11	1	$CH_2NHCOMe$	OH
12	1	$CH_2NHCOEt$	OH
13	1	$CH_2NHCOPr$	OH
14	1	$CH_2NHCOPr-i$	OH
15	1	$CH_2NHCOBu$	OH
16	1	$CH_2NHCOBu-t$	OH
17	1	$CH_2NHCO-Hep$	OH
18	1	$CH_2NHCOCH(Et)(Bu)$	OH
19	1	$CH_2NHCOCH_2CH_2Ph$	OH
20	1	$CH_2NHCOCH=CHPh$	OH
21	1	$CH_2NHCOPh$	OH
22	2	CN	OH
23	2	CN	OEt
24	2	CH_2NH_2	OH
25	2	$CH_2NHCOMe$	OH
26	2	$CH_2NHCO-undecyl$	OH
27	2	$CH_2NHCOCH=CHPh$	OH
28	2	$CH_2NHCOPh$	OH
29	2	COOEt	OH
30	2	COOEt	OEt
31	2	$NH_2 \cdot HCl$	OH

[0036]
[Table 2]



(4)

化合物番号	R^7	R^8	R^9	R^{10}
32	CN	OH	H	H
33	CN	OH	Me	H
34	CN	OH	Me	Me
35	CN	OEt	H	H
36	CN	OEt	Me	H
37	CN	OEt	Me	Me
38	COOEt	OEt	H	H
39	COOEt	OEt	Me	H
40	NH_2	OH	cycl-Pr	H

[0037] The example 1 of a trial: Each cut to an even length the carnation (form: Nora, Dianthus caryophyllus, "Nora") which just which used the carnation carried out the cut-flowers freshness maintenance effectiveness test harvest by 20cm of lower twists of the piece of **, and the thing except the adhesion leaf of Section 1 was prepared the bottom. It considered as 5mM solutions of a sample offering compound with distilled water, and the sodium hydrogencarbonate neutralized, respectively. The 70ml was put into the vial which put four carnations, in order to prevent the evaporation from an oil level, it covered on the lap, and it set to the thermostatic chamber of 24 degrees C and 2000Lux. Distilled water was given after the carnation inhaled all the sample solutions. The ****** days after processing estimated the freshness maintenance effectiveness. Moreover, it investigated also about the phytotoxicity over forage. A result is shown in Table 3.

[0038]

[Table 3]

供試化合物	日持ち日数	薬害
1	12	なし
2	14	なし
3	11	なし
4	9	なし
5	10	なし
6	12	なし
7	9	なし
8	11	なし
9	9	なし
11	10	なし
12	14	なし
13	13	なし
14	11	なし
16	13	なし
22	12	なし
32	8	なし
33	13	なし
34	14	なし
35	12	なし
36	9	なし
37	12	なし
38	8	なし
水+炭酸水素ナトリウム	5	なし
水のみ	7	なし

[0039] The example 2 of a trial: Each cut to an even length the carnation (form: Nora, Dianthus caryophyllus"Nora") which just which used the carnation carried out the cut-flowers freshness maintenance effectiveness test harvest by 20cm of lower twists of the piece of **, and the thing except the adhesion leaf of Section 1 was prepared the bottom. It considered as 5mM solutions of a sample offering compound with distilled water, and the sodium hydrogencarbonate neutralized, respectively. The 70ml was put into the vial which put four carnations, in order to prevent the evaporation from an oil level, it covered on the lap, and it set to the thermostatic chamber of 22 degrees C and 2000Lux. Distilled water was given after the carnation inhaled all the sample solutions. The ****** days after processing estimated the freshness maintenance effectiveness. Moreover, it investigated also about the phytotoxicity over forage. A result is shown in Table 4.

[0040]

[Table 4]

A sample offering compound Keeping days Phytotoxicity 2 14 Nothing 11 14 Nothing 18 10 Nothing 22 14 Nothing 28 10 Nothing 31 14 Nothing Water + sodium hydrogencarbonate 7 Nothing Only water With no 8 [0041]

[Effect of the Invention] In this invention, the freshness maintenance effectiveness of cut flowers is high, the load to an environment is mitigated, and it is cheap and, moreover, the new compound of the freshner for cut flowers with little generating of phytotoxicity and these freshners or its salt can be obtained.

[Translation done.]

* NOTICES *

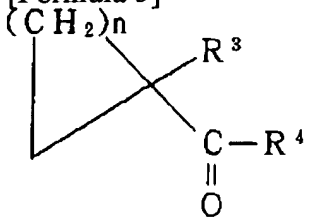
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2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

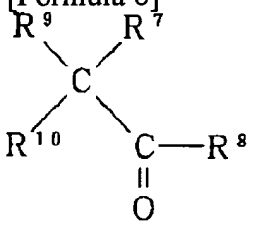
[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the new compound of the freshner for cut flowers which used the cycloalkane derivative, the carboxylic-acid derivative, this derivative, etc., and these freshners, or its salt.
[0002]
[Description of the Prior Art] A petal and a leaf will wither, ****** will advance as a freshness fall begins from immediately after flower-gathering and cut flowers follow a day, and appreciation worth of **** will be lost soon. For example, if 10 day will pass from one week after harvest in the carnation currently consumed 700 million per year also in cut flowers, a petal will age rapidly with the rapid increment in endoecism ethylene (withering). In the flowering plant industry, prevention of freshness degradation of the cut flowers to which need will be expanded increasingly from now on is a very important technical problem, and in order to solve this technical problem, various freshners are used For example, the carnation which has appeared on the market in the commercial scene in recent years is processed for the purpose of freshness maintenance with the thiosulfuric-acid silver which is an ethylene operation inhibitor. Thiosulfuric-acid silver is used to many ethylene susceptibility cut flowers besides the carnation, and it can be said that it is an indispensable freshner in current flowering plant industry
[0003]
[Problem(s) to be Solved by the Invention] However, thiosulfuric-acid silver contains the complex ion which is a heavy metal ion, and, also internationally, development of the alternative freshner by which the environmental load was reduced due to concern of the environmental pollution by complex ion is called for in recent years. Development of various freshners is made in order to replace the basis of this background, and thiosulfuric-acid silver, and the alpha-aminoisobutyric acid, an AROKORONAMIN acid, or cis-propenyl phosphonic acid is proposed as a freshner for cut flowers until now. However, the alpha-aminoisobutyric acid is very expensive and lacking in practicality, and since an AROKORONAMIN acid is difficult to compound, it is difficult to industrialize. Moreover, cis-propenyl phosphonic acid is not put in practical use from there being phytotoxicity of a leaf etiolating. That is, the present condition is that what an environmental load is reduced compared with thiosulfuric-acid silver, and generating of phytotoxicity can moreover still satisfy enough industrially few as a freshner which can be manufactured is not obtained. The technical problem of this invention has the high freshness maintenance effectiveness of cut flowers, and the load to an environment is mitigated, and it is cheap and is in moreover offering the new compound of the freshner for cut flowers with little generating of phytotoxicity, and these freshners, or its salt.
[0004]
[Means for Solving the Problem] This invention relates to the new compound of the freshner for cut flowers characterized by the thing which is chosen as the carboxylic-acid derivative list expressed with the cycloalkane derivative and general formula (4) which are expressed with a general formula (3) from these salts, and which contain a kind as an active principle at least, and these freshners, or its salt.

[0005]
[Formula 5]



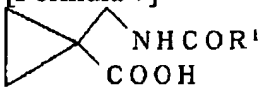
(3)

(n shows 1 or 2 among a formula, and R3 show a hydrogen atom, the amino group, a cyano group, -C (O) R5, or CH2-NHR6.) R4 shows a hydroxyl group, C1 - 4 alkoxy groups, the amino group, or an ANIRINO radical. R5 shows a hydroxyl group, C1 - 4 alkoxy groups, or the amino group. R6 shows a hydrogen atom, C1 - 11 alkyl carbonyl group, phenethyl carbonyl, styryl carbonyl, or benzoyl. However, R4 is not a hydroxyl group, when n is 1 and R3 are an amino group.
[0006]
[Formula 6]



(4)

(R7 shows a cyano group, the amino group, or C1 - 4 alkoxy carbonyl group among a formula.) R8 shows a hydroxyl group, or C1 - 4 alkoxy groups. R9 and R10 are the same -- or it differs and a hydrogen atom, or C1 - 4 alkyl groups is shown.
[0007]
[Embodiment of the Invention] Said general formula (1) In the compound of - (4), the example of each radical shown by R1-R10 is as follows. As C1 - 4 alkyl groups, methyl, ethyl, propyl, isopropyl, cyclo propyl, butyl, isobutyl, sec-butyl, tert-butyl, cyclo butyl, etc. are mentioned. In addition to said C1 - 4 alkyl groups, as C1 - 8 alkyl groups, pentyl, hexyl, cyclohexyl, heptyl, an octyl radical, etc. are mentioned. In addition to said C1 - 4 alkyl groups, and said C1 - 8 alkyl groups, nonyl, DESHIRU, an undecyl radical, etc. are mentioned as C1 - 11 alkyl groups. As C1 - 4 alkoxy groups, methoxy and ethoxy ** propoxy, isopropoxy, and a butoxy radical are mentioned. As C1 - a 4 alkoxy carbonyl group, methoxycarbonyl, ethoxycarbonyl, propoxy carbonyl, isopropoxycarbonyl, a butoxycarbonyl radical, a tert-butoxycarbonyl radical, etc. are mentioned. As a salt, sodium salt, potassium salt, ammonium salt, a hydrochloride, a sulfate, etc. can be illustrated. Although some of said compounds were known compounds, they were not known about all having the freshness maintenance effectiveness to cut flowers. Moreover, it is as follows reference a non-indicated compound among said compounds. The compound expressed with a general formula (1), and its salt (compound of claim 1).
[0008]
[Formula 7]



(1)

(R1 shows C1 - 8 alkyl groups, a phenyl group, a phenethyl radical, or a styryl radical among a formula.)
[0009] The compound of a general formula (1) is compounded by the amidation reaction usually performed, when it can manufacture by various approaches and 1-aminomethyl cyclopropane carboxylic acid is used as starting material. For example, it is acid halide to 1-aminomethyl cyclopropane carboxylic acid. R1COX (inside of a formula [R1 is the same as the above.]) X shows a halogen atom

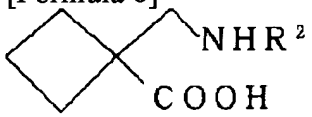
The approach of making it react is mentioned. Usually, about 0.5-5 mols of latters are used to one mol of former. In this reaction, it is desirable to make a base live together in order to remove the halide acid to generate. As a base to be used, a well-known thing can be used widely conventionally, for example, organic metal bases, such as inorganic bases, such as organic bases, such as triethylamine, pyridine, 4-N, and N-dimethylamino pyridine and N.N-dimethylaniline, a sodium hydroxide, and potassium carbonate, butyl lithium, and a lithium diisopropyl amide, sodium acetate, etc. can be illustrated. Moreover, although it changes also with classes of base used as a solvent Generally an inert solvent is desirable For example, aromatic hydrocarbon, such as benzene, toluene, and a xylene Pyridines, such as a pyridine and picoline, dichloromethane, chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane, tetrachloroethylene, Halogenated hydrocarbon, such as a trichloroethylene, chlorobenzene, and o-dichlorobenzene Ether, such as aprotic polar solvents, such as aliphatic hydrocarbon, such as n-hexane, N.N-dimethylformamide, and dimethyl sulfoxide, diethylether, a tetrahydrofuran, and dioxane, water, or these mixed solvents are mentioned. -20-100 degrees C, preferably, this reaction is a temperature requirement 0 degree C - near a room temperature, and is usually ended in about 0.1 - 24 hours.

[0010] 1-cyano cyclopropane phenyl amide (compound of claim 2).

This compound is manufactured by the amidation reaction usually performed, when it can manufacture by various approaches and 1-cyano cyclopropane carboxylic acid is used as starting material. For example, the approach to which the acid halide which inorganic halogenides, such as a phosphoryl chloride, a thionyl chloride, a phosphorus pentachloride, and a phosphorus trichloride, are made to act, and is obtained in 1-cyano cyclopropane carboxylic acid, and an aniline are made to react is mentioned. The base and solvent which are used for a reaction, the amount of the reaction agent used, reaction temperature, and reaction time are the same as that of the above-mentioned amidation reaction. At the reaction of acid halide and an aniline, by using an aniline more than the amount of 2 double, even if it does not use a base in addition to this, it can manufacture. The compound expressed with a general formula (2), and its salt (compound of claim 3).

[0011]

[Formula 8]



(2)

(A hydrogen atom, C1 - 11 alkyl carbonyl group, a styryl carbonyl group, or benzoyl is shown by the inside R2 of a formula.)

[0012] R2 among the compounds of a general formula (2) The compound (1-aminomethyl cyclobutanecarboxylic acid) which is a hydrogen atom is compounded by the reduction reaction of nitril usually performed, when it can manufacture by various approaches and 1-cyano cyclobutanecarboxylic acid is used as starting material. For example, it is manufactured by using metallic hydrogen complex compounds, such as a lithium aluminum hydride, for 1-cyano cyclobutanecarboxylic acid, or carrying out contact hydrogenation using the catalyst of a Raney nickel catalyst, Raney cobalt, diacid-ized platinum, etc. In the reduction reaction using a metallic hydrogen complex compound, ether, such as diethylether and a tetrahydrofuran, is usually used for a solvent, and a desiccation solvent is desirable. In the contact hydrogenation reaction using a catalyst etc., alcohol, ammonia saturated alcohol, an acetic acid, etc. are usually used for a solvent. R2 R2X among the compounds of a general formula (2) C 1-11 The compound which is an alkyl carbonyl group, a styryl carbonyl group, or benzoyl is acid halide to 1-aminomethyl cyclobutanecarboxylic acid. (inside of a formula [R2 is the same as the above.]) X A halogen atom is shown. It can manufacture by making it react. The solvent to be used, a base, reaction temperature, reaction time, etc. are the same as that of the time of manufacture of the compound shown by the above-mentioned general formula (1).

[0013] Among the compounds used as an active principle of the freshner of this invention, the thing except said and its salt are known compounds, are commercially available or can be easily obtained to J.Chem.Soc., 75,921-927 (1899), etc. by the approach of a publication etc. The freshner of this invention

is manufactured by dissolving the above-mentioned active principle in a suitable solvent with a suitable surfactant and other suitable components if needed. Although the freshner of this invention can be used with the gestalt of a water solution, organic solvents, such as ethanol, may be used for it and it may usually use these together. Moreover, medicine is manufactured by the shape of powder, granularity, and a tablet, and at the time of use, it may be made to dissolve in water and you may use. Although the concentration of an active principle is suitably defined according to conditions, such as a class of object flowering plant, an art, and the processing time, it is usually 0.1-100mM, and in the case of after treatment, it is desirable to make it into 1 - 100mM extent in 0.1 - 50mM and pretreatment.

[0014] As a surface active agent which can be used for the freshner of this invention, alkylbenzene sulfonates, fatty alcohol sulfate, alkyl trimethylammonium chloride, a betaine mold compound, sodium lauryl sulfate, a naphthalene formaldehyde condensate, polyoxyethylene sorbitan monooleate, polyoxyethylene SUCHIRIRUE-Tell, polyoxyethylene RAURIRUE-Tell, polyoxyethylene nonyl phenyl ether, a polyoxyethylene polyoxypropylene blockpolymer, sucrose fatty acid ester, etc. are mentioned, for example. As concentration of a surfactant, although suitably set by the class, the object flowering plant, the art, and the processing time of a surfactant, generally in the case of after treatment, in about 3-1000 ppm and pretreatment, it is about about 3-300 ppm. Moreover, the freshner of this invention can be made to contain the component of sedimentation agents, such as pH regulators, such as plant growth regulators, such as parts for micronutrient, such as nutrients, such as nitrogen, Lynn, a potassium, and cane sugar, iron, zinc, manganese, copper, and boron, B-nine (DAMINOJIDDO), and a benzyladenine, and a sodium hydrogencarbonate, and an aluminum sulfate, other freshners, a color coupler, a germicide, antiseptics, and others.

[0015] On the occasion of use of the freshness processing agent of this invention, that what is necessary is just to immerse the cut end of cut flowers in the freshner of this invention, since special processing is not needed, anyone can carry out in various scenes easily. The method of keeping [immerse / in this invention freshner / the cut end of cut flowers] made or the approach in which only fixed time amount is made immersed is more specifically mentioned. The former is an approach called the so-called after treatment adopted when arranging cut flowers in the vase at the case where cut flowers are very sold to containers, such as a bucket, at a store etc., the home, the exhibition, etc., and the latter is an approach by which a flowering plant production contractor is called after [harvest] fixed time amount, for example, the so-called pretreatment as which it is adopted when performing drugs processing for about 4 to 24 hours and shipping after that. In addition, the freshner of this invention can be used by the leaf, spray processing to a petal, etc.

[0016] Although there is especially no limit as object flowering plants of the freshner of this invention and it is effective in various kinds of flowering plants For example, a carnation, SUITOPI -, SUKASHIYURI, a European monkshood, A butterfly weed, HANATORANOO, Delphinium, HANAAOI, contribution NYURA, A bleeding heart, a veronica, you FORU beer full GENSU, astro-MERIA, A freesia, a mustached pink, snapdragon, a gypsy rose, a stock, When it uses for Gypsophila elegans, a bougainvillea, a geranium, KARUSE ora rear ** ******, ****-****, BUBARUDIA, grotesque RIOSA, cosmos, RISHIANSASU, a dahlia, a fuchsia, SANTAKA, etc., remarkable effectiveness is especially done so.

[0017]

[Example] The example of reference, the example of manufacture, and the example of a trial are given to below, and this invention is explained to it still more concretely.

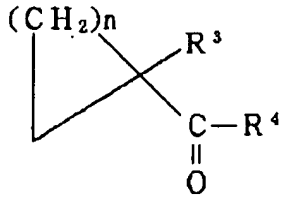
Example 1 of reference Contact hydrogenation of the 1-cyano cyclopropane carboxylic-acid (2)1g (9 millimol) was carried out in ordinary temperature and ordinary pressure under diacid-ized platinum existence for 30 hours among the synthetic acetic-acid solvent of 1-aminomethyl cyclopropane carboxylic acid (10). Cerite filtration of the reaction mixture is carried out, vacuum concentration of the toluene is added and carried out to filtrate, and it is a yellow rough crystal. 1.4g was obtained. This thing was ******ed from the methanol and the 538mg colorless crystal was obtained. (52% of yield) The melting point [a reference value and 238 degrees C (decomposition)] of 235 degrees C (decomposition) IR(KBr) numax(cm-1):3250-2250 (NH3+), 1620 (deltaasNH3+), 1570 (nuasCOO-), 1520

(deltaasNH3+), 1400 (nusCOO-), 1250 and 1110, 8601 H-NMR(CD3OD):delta0.69-0.72 (2H, m), and 1.16- 1.19 (2H, m) and 3.30 (2H, s, CH3)
[0018] Example 1 of manufacture Synthetic 1-cyano cyclopropane carboxylic-acid (2)1.67g and the thionyl chloride of 1-cyano cyclopropane phenyl amide (5) 15ml was mixed and the heating ring current was performed for 4 hours. To this solution, it is anhydrous toluene. Aniline dissolved in 30ml 4.0g (43 millimol) was added and heating churning was carried out for 1 hour. Then, water was cooled and poured and the organic layer was washed in order of a hydrochloric acid, 10% sodium hydroxide, and water 5%. It dried, vacuum concentration of the organic layer was carried out, and the brown rough crystal was obtained. It recrystallized [toluene] and the 0.30g colorless crystal was obtained. (11% of yield)
Melting point 90 degree-CIR(KBr) numax(cm-1):3250(NH), 3050 and 2240 (CN), 1670 (C=O, amide), 1600, 1540, 1490, 1450, 1330, 1250, 1180 and 1080, 9701 H-NMR(CD3OD):delta1.60-1.72 (4H, m), 7.13-7.54 (5H, m, Ph)
[0019] Example 2 of manufacture Acetic acid which added and distilled the acetic anhydride of 0.5% w/w of composition of 1-acetamido methyl cyclopropane carboxylic acid (11) It is diacid-ized platinum to 15ml. 20mg and 1-cyano cyclopropane carboxylic acid 1g (9 millimol) was added and contact hydrogenation was carried out over 30 hours in room temperature 1atm. A product is filtered, filtrate is condensed and it is a yellow rough crystal. 1.2g was obtained. This thing was ******ed from chloroform and the 353mg colorless crystal was obtained. (25% of yield)
Melting point 164 degree-CIR(KBr) numax(cm-1):3600-2300 (COOH), 1710 (C=O, carboxyl), 1680 (C=O, amide), 1540, 1400, 1260 (C-N), 1130 (C-O)
1 H-NMR(CD3OD): 1.95 (3H, s, CH3) delta0.9-0.95 (2H, m), 1.18-1.22 (2H, m), 3.31 (2H, s, CH2)
[0020] Example 3 of manufacture The tetrahydrofuran was added and agitated to synthetic 1-aminomethyl cyclopropane carboxylic acid (10) of 1-benzoyl aminomethyl cyclopropane carboxylic acid (21). It is water to this. Sodium hydroxide dissolved in 3.41ml 1.37g is added, and it continues and is a benzoyl chloride. 2.11ml was added. After agitating for 30 minutes at a room temperature, concentrated hydrochloric acid was added at 0 degree C, it was made acidity, and ethyl acetate extracted after irrigation. The organic layer was doubled, saturation brine washed and it was made to dry with sulfuric anhydride magnesium. Vacuum concentration is carried out and it is a light yellow rough crystal. 2.88g was obtained. This was ******ed from the hexane-ether and the 1.31g crystal was obtained.
Melting point 190-190.5 degree-CIR(KBr) numax(cm-1):3370(NH), 3200- 2500 (COOH) and 1690 (C=O, carboxyl) -- 1610 (C=O, amide), 1540, 1420, 1240 (C-N), 1170 (C-O), 1030 (C-N), 9001 H-NMR(CD3OD):delta1.02 (2H, q, CH2), 1.23 (2H, q, CH2), 3.61 (2H, s, CH2), 7.40-7.53 (5H, m, C6H5)

[0021] It replaces with example of manufacture 4 benzoyl chloride. A chlorination propionyl, the chlorination n-butyryl, Chlorination isobutyryl, chlorination pivaloyl, chlorination 2-ethyl hexa noil. The phenylacrylyl chloride was used and also it is made to be the same as that of the example 1 of manufacture. 1-propionyl aminomethyl cyclopropane carboxylic acid (12), 1-butyryl aminomethyl cyclopropane carboxylic-acid (13) 1-isobutyryl aminomethyl cyclopropane carboxylic-acid (14), 1-pivaloyl aminomethyl cyclopropane carboxylic-acid (16) 1-ECHIRUHEKISANOIRU aminomethyl cyclopropane carboxylic-acid (18) and 1-cinnamoyl aminomethyl cyclopropane carboxylic acid (20) were manufactured.
[0022] 1-propionyl aminomethyl cyclopropane carboxylic acid (12)
Colorless crystal IR(KBr) numax(cm-1):3350(NH), 3050- 2850 (COOH) and 1690 (C=O, carboxyl) -- 1620 (C=O, amide), 1540, 1460, 1420, 1310, 1240 (C-N), 1180 (C-O), 1100, 1030, 960, 9201 H-NMR (CD3OD):delta1.07 (2H, m), 1.16 (3H, t, CH2), 1.32 (2H, m), 2.23 (2H, q, CH2), 3.42 (2H, d, CH2)
[0023] 1-butyryl aminomethyl cyclopropane carboxylic acid (13)
Colorless crystal IR(KBr) numax(cm-1):3300(NH), 3100 (COOH), 2950, 1620 (C=O, carboxyl), 1560 (C=O, amide), 1420, 1270, 1220 (C-N), 2.32 (2H, t, CH2) 1110, 1060, 1020, 905, 800, 770, 6101 H-NMR(CDCl3):delta0.96 (3H, t, CH3), 1.04-1.33 (4H, m), 3.41 (2H, d, CH2)

[0024] 1-isobutyryl aminomethyl cyclopropane carboxylic acid (14)
Colorless crystal IR(KBr) numax(cm-1):3340(NH), 2960-2870, and 2580- 2540 and 1680 (COOH) -- 1620 (C=O, amide), 1560, 1470, 1420, 1310, 1230, 1190, 1100 (C-N), 1040, 960, 900, 865, 750, 680, 5801 H-NMR(CDCl3):delta1.08 (2H, m), 1.16 (6H, d, 2CH3), 1.33 (2H, m), 2.36 (1H, m, CH), 3.42 (2H, d, CH2)
[0025] 1-pivaloyl aminomethyl cyclopropane carboxylic acid (16)
Colorless crystal IR(KBr) numax(cm-1):3350(NH), 2950, 2600, 1690 (C=O, carboxyl), 1640 (C=O, amide), 1530, 1450, 1420, 1360, 1340, 1290, 1260, 1200, 1080 (C-N), 1030, 950, 910, 850, 640, 5301 H-NMR(CDCl3):delta1.07 (2H, m), 1.20 (9H, s), 1.32 (2H, m), 3.42 (2H, d, CH2)
[0026] 1-ECHIRUHEKISANOIRU aminomethyl cyclopropane carboxylic acid (18)
colorless liquefied object IR(film) numax(cm-1): -- 3340 (NH), 3250-2700 (COOH), and 2250, 1700 (C=O, carboxyl), 1620 (C=O, amide), 1540, 1460, 1420, 1370 and 1180 (C-O)
1 H-NMR(CD3OD): 3.44 (2H, d, CH2) delta1.09 (2H, m, CH2), 7.28 (1H, br, OH)
[0027] 1-cinnamoyl aminomethyl cyclopropane carboxylic acid (20)
White crystalline melting point 245-255.5 degree-CIR(Kbr) numax(cm-1):3370(NH), 3250-2300 (COOH), 1680 (C=O, carboxyl), 1590 (C=O, amide), 1490, 1420, 1220 (C-N), 1170 (C-O)
1 H-NMR(CD3OD): delta0.99 (2H, q, CH2), 1.23 (2H, q, CH2), 3.52 (2H, q, CH2), 6.65 (H, s, CH), 6.72 (H, s, CH), 7.30-7.60 (5H, m, C6H5)
[0028] Example 5 of manufacture Contact hydrogenation of the 1-cinnamoyl aminomethyl cyclopropane carboxylic-acid (20) 0.5g (2 millimol) was carried out in a room temperature and 1atm under existence of the synthetic diacid-ized platinum catalyst of 1-phenyl propionylamino MECHIRUSHIKUROPUROPAN carboxylic acid (19), and in 7ml of acetic acids. 20 hours after, after filtering reaction mixture, vacuum concentration was carried out and the 247mg yellow crystal was obtained.
Melting point 41 degree-CIR(KBr) numax(cm-1):3370(NH), 3300-2300 (COOH), 1690 (C=O, carboxyl), 1620 (C=O, amide), 1540, 1420, 1240 (C-N), 1190 (C-O)
1 H-NMR(CD3OD): delta2.85 (2H, t, CH2), 2.95 (2H, t, CH2), 3.10 (2H, s, CH2), 7.10-7.30 (5H, m, C6H5)
[0029] Example 6 of manufacture Sequential addition of the synthetic diacid-ized platinum catalyst of 1-aminomethyl cyclobutanecarboxylic acid (24), 7ml (what was distilled simply) of acetic acids, and the 1-cyano cyclobutanecarboxylic acid (23) 1.0g (8 millimol) was carried out, and contact hydrogenation was carried out in a room temperature and 1atm. 25 hours after, after filtering reaction mixture, vacuum concentration was carried out and the 0.72g white crystal was obtained. (70% of yield)
Melting point 195-197 degreeCIR(KBr) numax(cm-1):3400-2280 (NH3+), 2180, 1620 (deltaasNH3+), 1560 (nuasCOO-), 1510 (deltasNH3+), 1390 (nusCOO-), 1250, 1180, 11301 H-NMR(D2O):delta1.88-2.05 (4H, m), and 2.32- 2.44 (2H, m) and 3.28 (2H, s, CH2)
[0030] Example 7 of manufacture Synthetic 1-aminomethyl cyclobutanecarboxylic acid (24) 0.5g (4 millimol) of 1-acetamide methyl cyclobutanecarboxylic acid (25), 0.61g (8 millimol) of acetyl chlorides, DMF10ml, and pyridine 10ml were added, and it agitated at the room temperature for 1 hour. Then, 3.5ml of concentrated hydrochloric acid was added by 0-degreeC, it was made acidity, 20ml of water was put in, and ethyl acetate extracted. The organic layer was doubled, it washed and dried, and vacuum concentration was carried out and the 0.35g yellow liquid was obtained. The column chromatography (10:1 - ethyl acetate: hexane: ethyl-acetate = methanol = 10:1) refined this thing, and the 0.19g colorless liquid (25) was obtained. (28% of yield)
Melting point 140-141 degree-CIR(Kbr) numax(cm-1):3360(NH), 3300-2400 (COOH), 1690 (C=O, carboxyl), 1630 (C=O, amide), 1555, 1420, 1205 (C-O), 710 (C-N)
1H-NMR(D2O):delta1.88- 2.02 (4H, m), 1.96 (3H, s, CH3), and 2.30- 2.43 (2H, m) and 3.57 (2H, s, CH2)
[0031] Replaced with the example of manufacture 8 acetyl chloride, and chlorination lauroyl, the phenylacrylyl chloride, and the benzoyl chloride were used, respectively, and also 1-lauroyl aminomethyl cyclobutanecarboxylic acid (26) 1-cinnamoyl aminomethyl cyclobutanecarboxylic acid

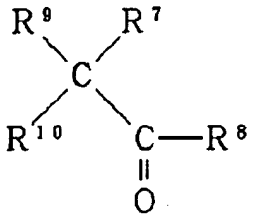
(27) and 1-benzoyl aminomethyl cyclobutanecarboxylic acid (28) were compounded like the example 7 of manufacture.
[0032] 1-lauroyl aminomethyl cyclobutanecarboxylic acid (26)
light yellow crystalline melting point 45degree-CIR(KBr) numax(cm-1): -- 3310 (NH), 3200-2700 (COOH), and 1700 (C=O, carboxyl), 1640 (C=O, amide), 1540, 1460, 1430, 1380, 1240 (C-N) and 1210 (C-O)
1 H-NMR(CD3OD):delta1.90-2.03 (4H, m) and 2.33- 2.42 (2H, m) and 3.32 (2H, m, CH2)
[0033] 1-cinnamoyl aminomethyl cyclobutanecarboxylic acid (27)
Melting point 125-126 degree-CIR(KBr) numax(cm-1):3340(NH), 3220-2720 (COOH), 1690 (C=O, carboxyl), 1610 (C=O, amide), 1550, 1420, 1390, 1210 (C-O), 670 (C-O)
1 H-NMR(CDCl3): delta1.91-2.09 (4H, m), 2.39-2.46 (2H, m), 3.32 (2H, s, CH2), 7.34-7.41 (5H, m, C6H5)
[0034] 1-benzoyl aminomethyl cyclobutanecarboxylic acid (28)
light yellow crystalline melting point 116-116.5degree-CIR(KBr) numax(cm-1): -- 3430 (NH) -- 1900 333-2720 (COOH), 1700 (C=O, carboxyl), 1630 (C=O, amide), 1530, 1400, 1240 (C-N), 1160 (C-O), 8901 H-NMR(CDCl3):delta1.89-2.14 (4H, m), 2.39-2.47 (2H, m), 3.32 (2H, s, CH2), 7.40-7.52 (5H, m, C6H5)
The typical compound which can be used as an active principle of the freshner for cut flowers of this invention is shown in Table 1 and 2. in addition, a table -- setting -- Me -- methyl and Et -- in ethyl and Pr, heptyl and cycl-Pr show cyclo propyl and, as for propyl and Bu, Ph shows phenyl, as for butyl and Hep.
[0035]
[Table 1]



(3)

化合物番号	n	R^3	R^4
1	1	H	OH
2	1	CN	OH
3	1	CN	OEt
4	1	CN	NH_2
5	1	CN	NHPh
6	1	COOH	OH
7	1	COOH	OEt
8	1	COOH	NH_2
9	1	COOEt	OEt
10	1	CH_2NH_2	OH
11	1	$CH_2NHCOMe$	OH
12	1	$CH_2NHCOEt$	OH
13	1	$CH_2NHCOPr$	OH
14	1	$CH_2NHCOPr-i$	OH
15	1	$CH_2NHCOBu$	OH
16	1	$CH_2NHCOBu-t$	OH
17	1	$CH_2NHCO-Hep$	OH
18	1	$CH_2NHCOCH(Et)(Bu)$	OH
19	1	$CH_2NHCOCH_2CH_2Ph$	OH
20	1	$CH_2NHCOCH=CHPh$	OH
21	1	$CH_2NHCOPh$	OH
22	2	CN	OH
23	2	CN	OEt
24	2	CH_2NH_2	OH
25	2	$CH_2NHCOMe$	OH
26	2	$CH_2NHCO-undecyl$	OH
27	2	$CH_2NHCOCH=CHPh$	OH
28	2	$CH_2NHCOPh$	OH
29	2	COOEt	OH
30	2	COOEt	OEt
31	2	$NH_2 \cdot HCl$	OH

[0036]
[Table 2]



(4)

化合物番号	R^7	R^8	R^9	R^{10}
32	CN	OH	H	H
33	CN	OH	Me	H
34	CN	OH	Me	Me
35	CN	OEt	H	H
36	CN	OEt	Me	H
37	CN	OEt	Me	Me
38	COOEt	OEt	H	H
39	COOEt	OEt	Me	H
40	NH_2	OH	cycl－Pr	H

[0037] The example 1 of a trial: Each cut to an even length the carnation (form: Nora, Dianthus caryophyllus, "Nora") which just which used the carnation carried out the cut-flowers freshness maintenance effectiveness test harvest by 20cm of lower twists of the piece of **, and the thing except the adhesion leaf of Section 1 was prepared the bottom. It considered as 5mM solutions of a sample offering compound with distilled water, and the sodium hydrogencarbonate neutralized, respectively. The 70ml was put into the vial which put four carnations, in order to prevent the evaporation from an oil level, it covered on the lap, and it set to the thermostatic chamber of 24 degrees C and 2000Lux. Distilled water was given after the carnation inhaled all the sample solutions. The ****** days after processing estimated the freshness maintenance effectiveness. Moreover, it investigated also about the phytotoxicity over forage. A result is shown in Table 3.

[0038]

[Table 3]

供試化合物	日持ち日数	薬害
1	12	なし
2	14	なし
3	11	なし
4	9	なし
5	10	なし
6	12	なし
7	9	なし
8	11	なし
9	9	なし
11	10	なし
12	14	なし
13	13	なし
14	11	なし
16	13	なし
22	12	なし
32	8	なし
33	13	なし
34	14	なし
35	12	なし
36	9	なし
37	12	なし
38	8	なし
水+炭酸水素ナトリウム	5	なし
水のみ	7	なし

[0039] The example 2 of a trial: Each cut to an even length the carnation (form: Nora, Dianthus caryophyllus"Nora") which just which used the carnation carried out the cut-flowers freshness maintenance effectiveness test harvest by 20cm of lower twists of the piece of **, and the thing except the adhesion leaf of Section 1 was prepared the bottom. It considered as 5mM solutions of a sample offering compound with distilled water, and the sodium hydrogencarbonate neutralized, respectively. The 70ml was put into the vial which put four carnations, in order to prevent the evaporation from an oil level, it covered on the lap, and it set to the thermostatic chamber of 22 degrees C and 2000Lux. Distilled water was given after the carnation inhaled all the sample solutions. The ****** days after processing estimated the freshness maintenance effectiveness. Moreover, it investigated also about the phytotoxicity over forage. A result is shown in Table 4.

[0040]

[Table 4]

A sample offering compound Keeping days Phytotoxicity 2 14 Nothing 11 14 Nothing 18 10 Nothing 22 14 Nothing 28 10 Nothing 31 14 Nothing Water + sodium hydrogencarbonate 7 Nothing Only water With no 8 [0041]

[Effect of the Invention] In this invention, the freshness maintenance effectiveness of cut flowers is high, the load to an environment is mitigated, and it is cheap and, moreover, the new compound of the freshner for cut flowers with little generating of phytotoxicity and these freshners or its salt can be obtained.

[Translation done.]

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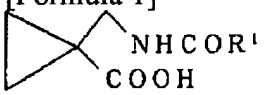
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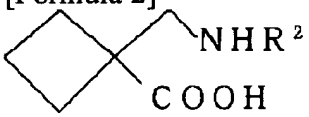
CLAIMS

[Claim(s)]
[Claim 1] The compound expressed with a general formula (1), and its salt.
[Formula 1]



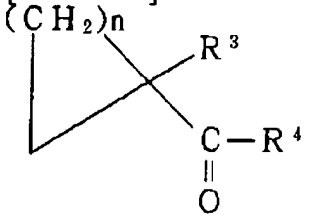
(1)

(R1 shows C1 - 8 alkyl groups, a phenyl group, a phenethyl radical, or a styryl radical among a formula.)
[Claim 2] 1-cyano cyclopropane phenyl amide.
[Claim 3] The compound expressed with a general formula (2), and its salt.
[Formula 2]



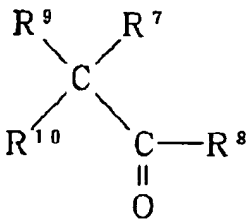
(2)

(A hydrogen atom, C1 - 11 alkyl carbonyl group, a styryl carbonyl group, or benzoyl is shown by the inside R2 of a formula.)
[Claim 4] The freshner for cut flowers characterized by the thing which is chosen as the carboxylic-acid derivative list expressed with the cycloalkane derivative and general formula (4) which are expressed with a general formula (3) from these salts, and which contain a kind as an active principle at least.
[Formula 3]



(3)

(n shows 1 or 2 among a formula, and R3 show a hydrogen atom, the amino group, a cyano group, -C (O) R5, or CH2-NHR6.) R4 shows a hydroxyl group, C1 - 4 alkoxy groups, the amino group, or an ANIRINO radical. R5 shows a hydroxyl group, C1 - 4 alkoxy groups, or the amino group. R6 shows a hydrogen atom, C1 - 11 alkyl carbonyl group, phenethyl carbonyl, styryl carbonyl, or benzoyl. However, R4 is not a hydroxyl group, when n is 1 and R3 are an amino group.
[Formula 4]



(4)

(R7 shows a cyano group, the amino group, or C1 - 4 alkoxy carbonyl group among a formula.) R8 shows a hydroxyl group, or C1 - 4 alkoxy groups. R9 and R10 are the same -- or it differs and a hydrogen atom, or C1 - 4 alkyl groups is shown.

[Claim 5] The freshner for cut flowers according to claim 4 whose cycloalkane derivative of a general formula (3) is 1-cyano cyclopropane carboxylic acid or 1-cyano cyclobutanecarboxylic acid.

[Translation done.]